생유기화학
(Bioorganic Chemistry)

Carbohydrates-II
(탄수화물-2)

Soonchunhyang University

Department of Chemical Engineering

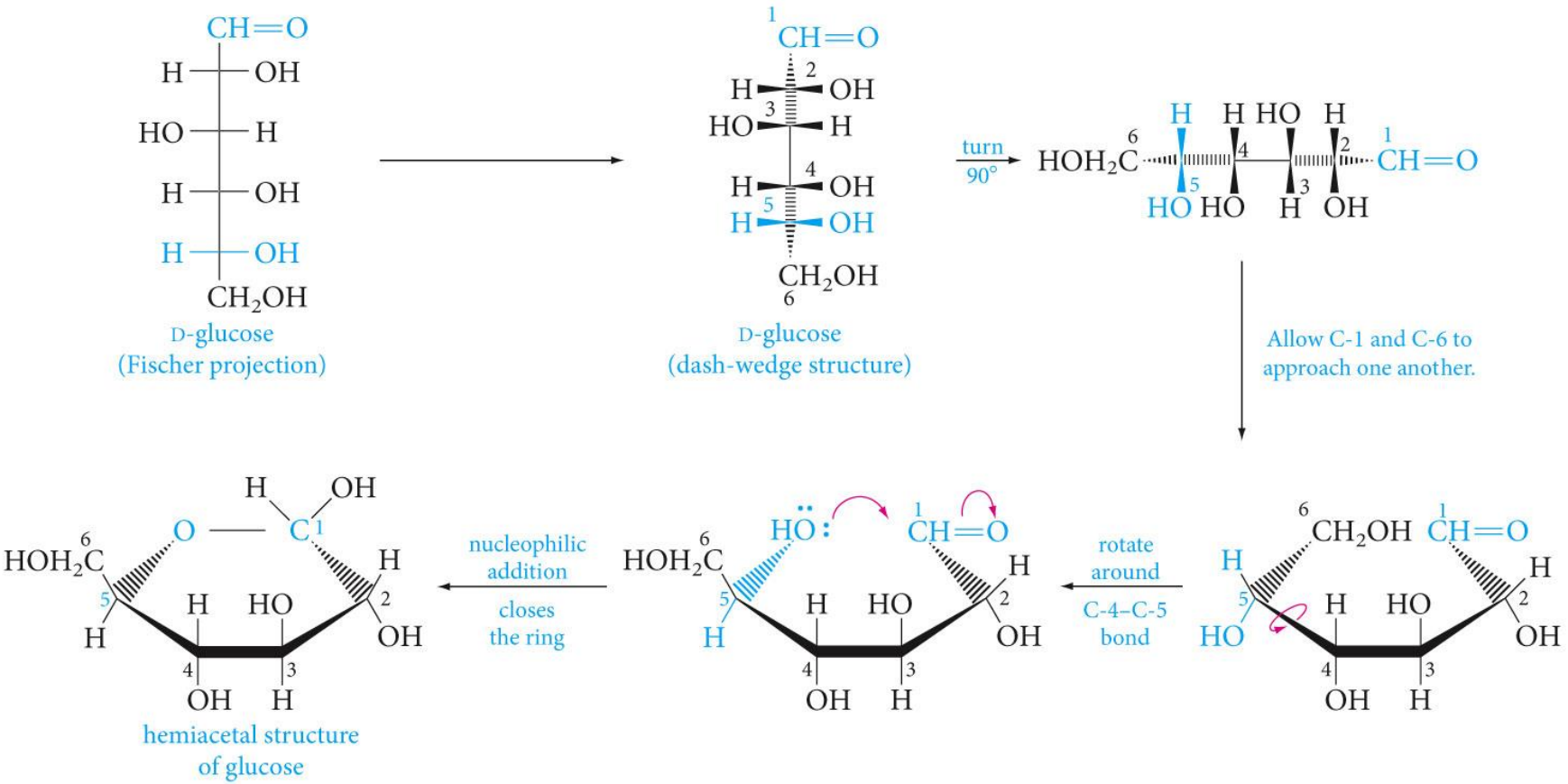
Prof. Jungkyun Im

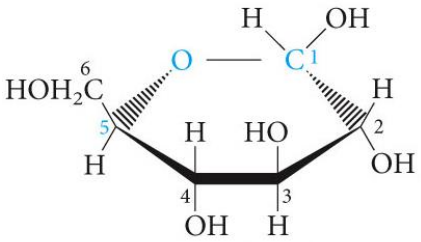
순천향대

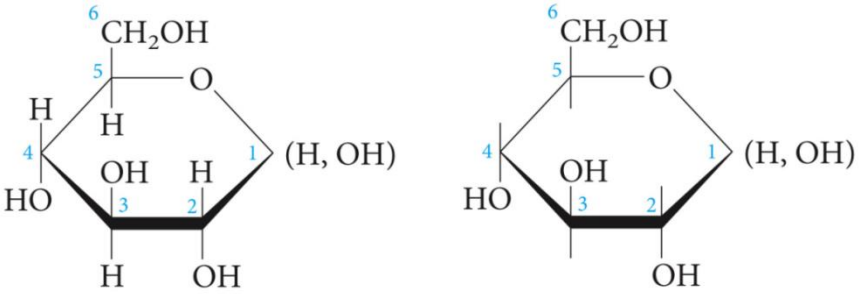
나노화학공학과

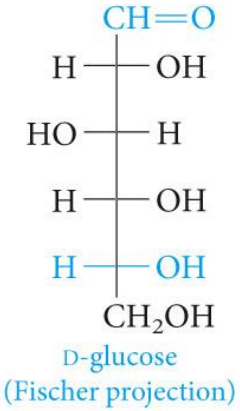
임 정 균 교수

4. The Cyclic Hemiacetal Structures of Monosaccharides



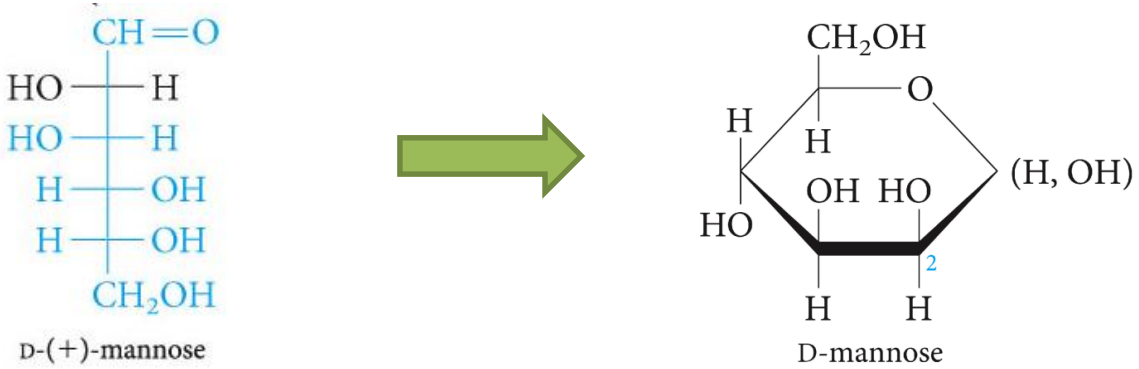




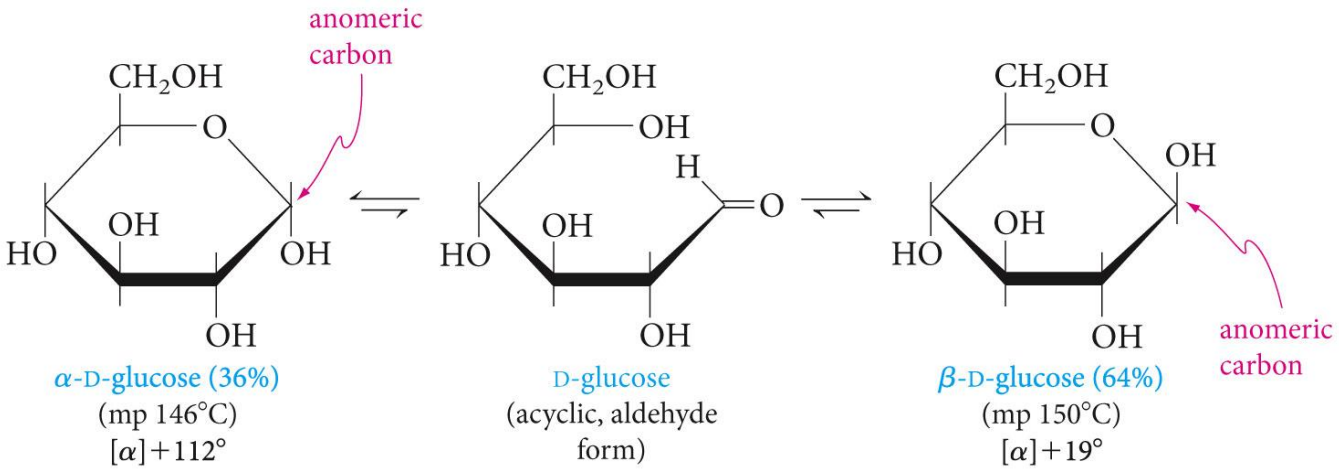


- Fischer projection에서 OH가 오른쪽에 있으면 Haworth projection에서는 ring 아래에 존재한다.
- D-sugar에서 CH_2OH는 ring위에 있다.

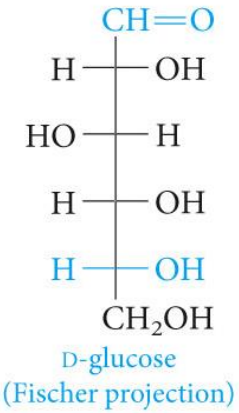
Example 3.
Draw the Haworth projection for the six-membered cyclic structure of D-mannose.



5. **Anomeric Carbon**s; Mutarotation



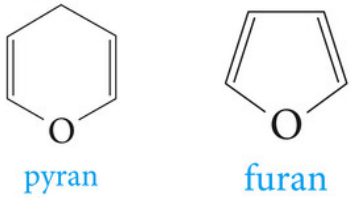
interconvert to each other in aqueous solution



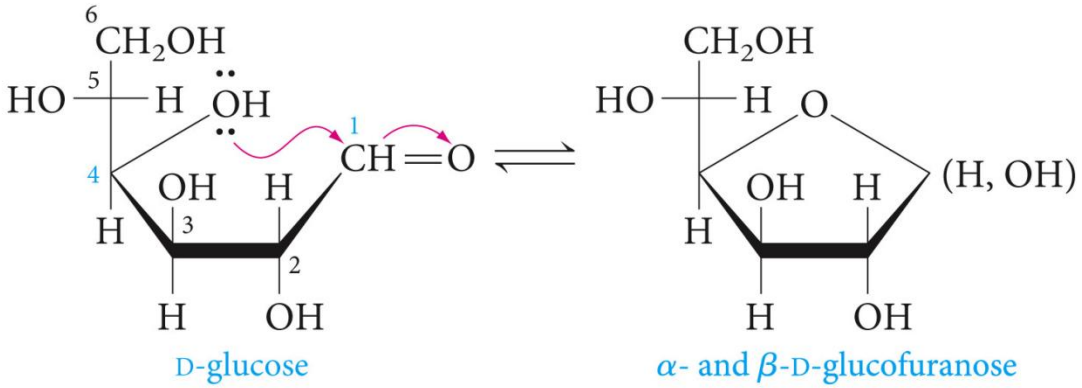
0.003% → silver mirror test

순수한 α-D-glucose를 물에 녹이면 specific rotation의 **초기값**은 112도 이지만 시간이 지남에 따라 52도가 된다. → why 52도? → example 16.4

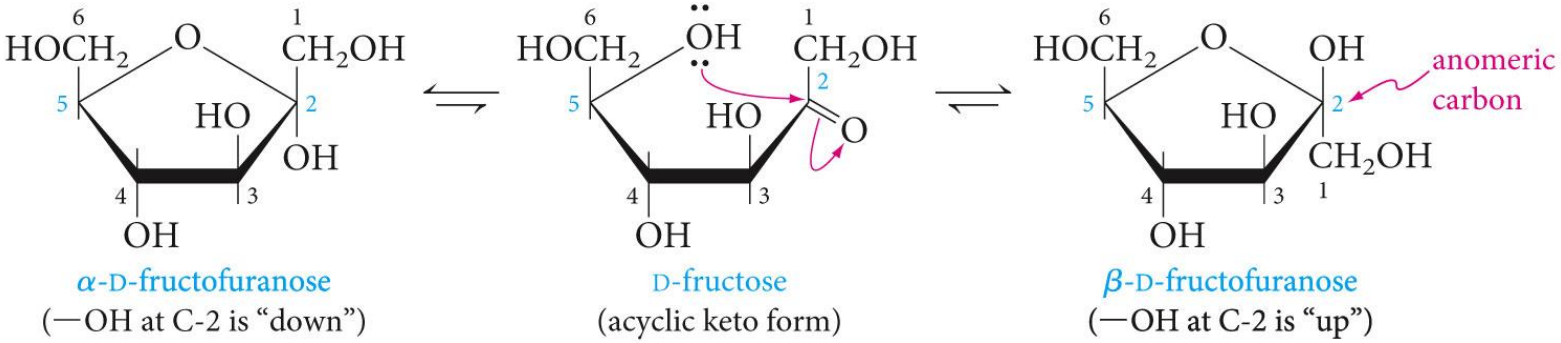
6. **Pyranose** and **Furanose** Structures



Pyranose: cyclic monosaccharide가 6각형일 때
Furanose: cyclic monosaccharide가 5각형일 때

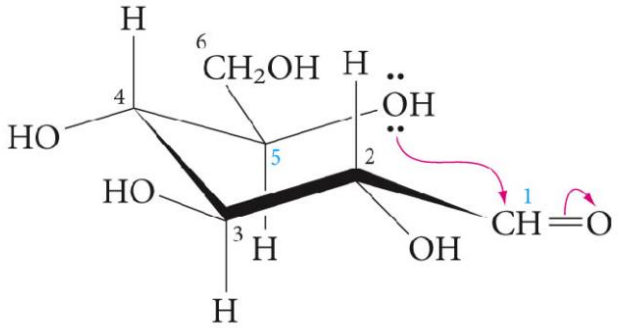


C5의 OH가 공격해서 hemiacetal이 되면 pyranose가 된다.

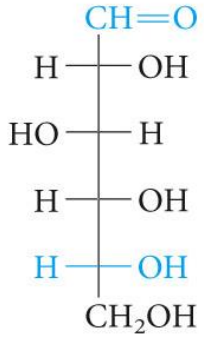


7. Conformations of Pyranoses

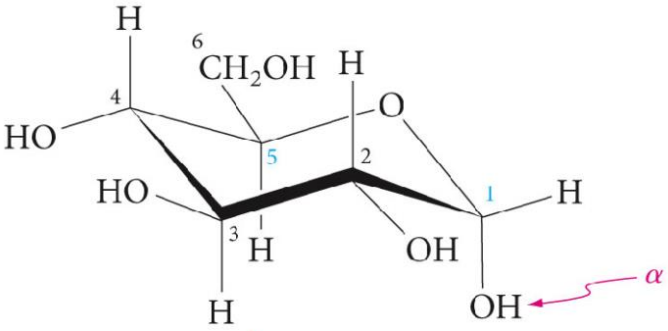
Pyranose rings prefer a chair conformation. We can rewrite the Haworth projection as below.



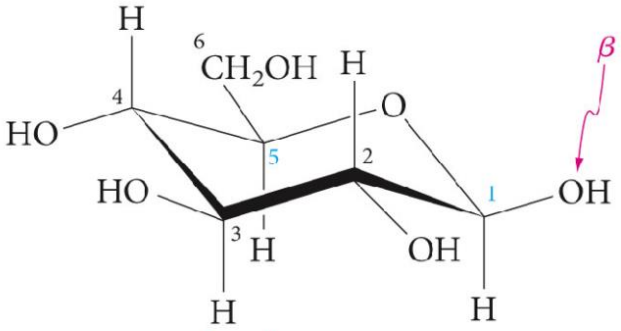
D-glucose
(acyclic, aldehyde form)



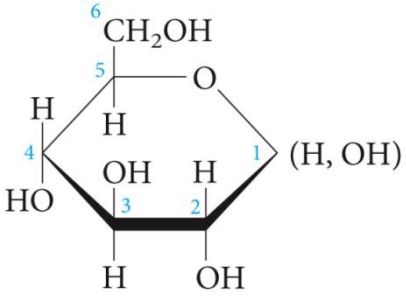
D-glucose
(Fischer projection)



α-D-glucopyranose



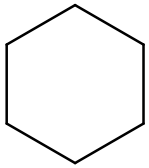
β-D-glucopyranose → alpha보다 더 abundant하다→ why?

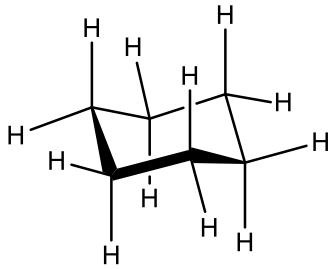


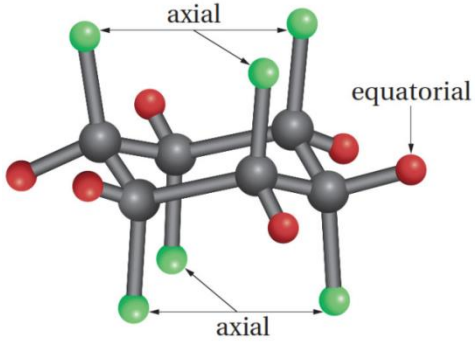
D-Glucose가 pyranose중에서 가장 stable하고 abundant하다. → why?

Larger substituents are equatorial.

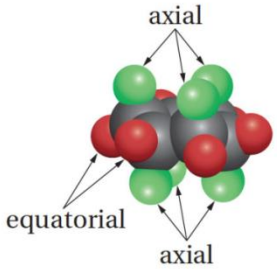
Conformational isomerism in Cyclohexane



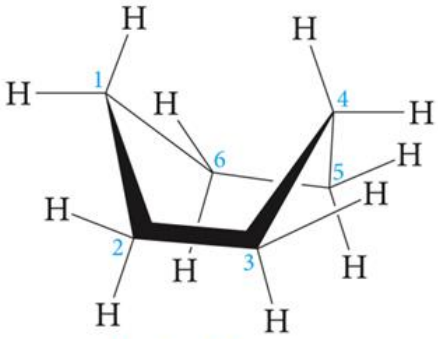




ball-and-stick model

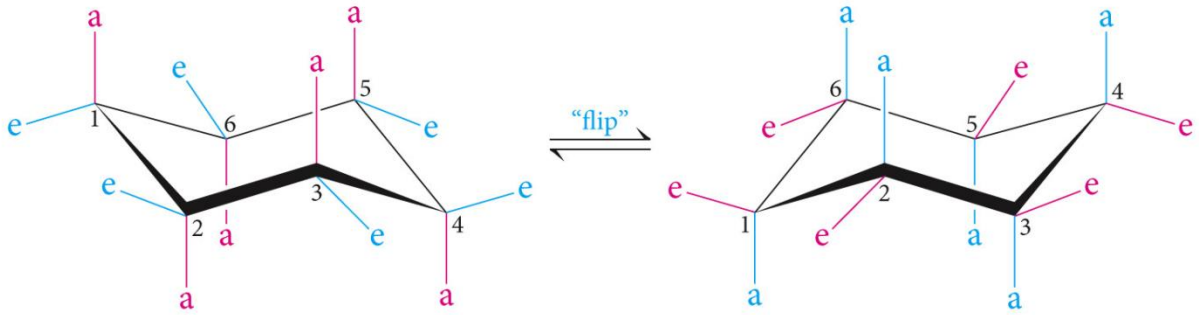


space-filling model

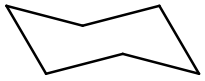


boat cyclohexane

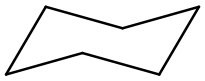
(not favored)

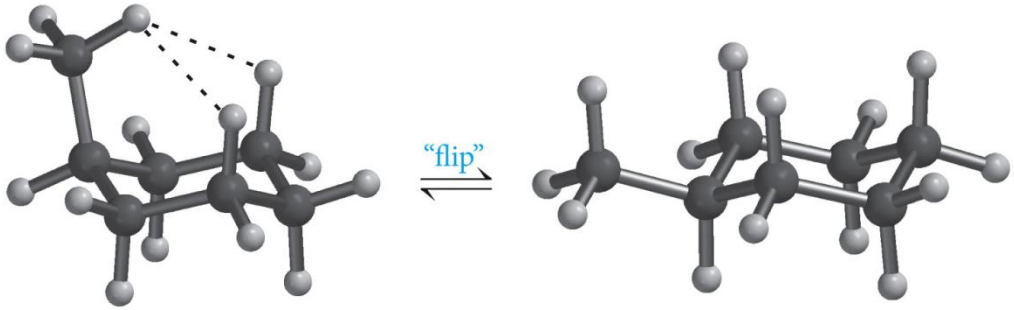


Axial bonds (red) in the left structure become equatorial bonds (red) in the right structure when the ring "flips."



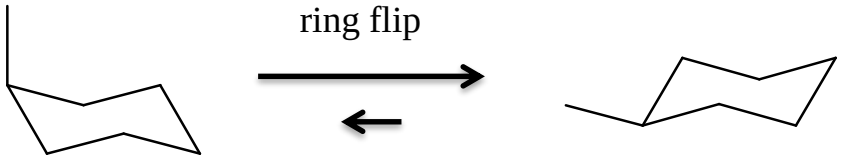
fast flipping at r.t,
slow flipping at -90°C





methyl axial
5%

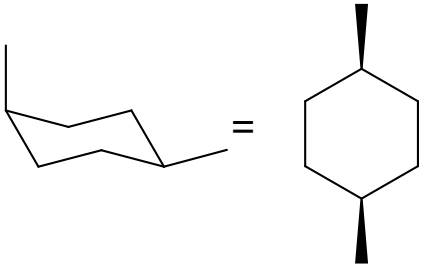
methyl equatorial
95%



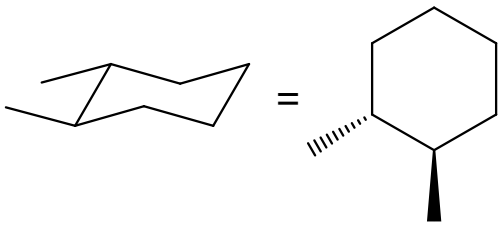
5%

95%

chloride, bromide등이 있어도 마찬가지..

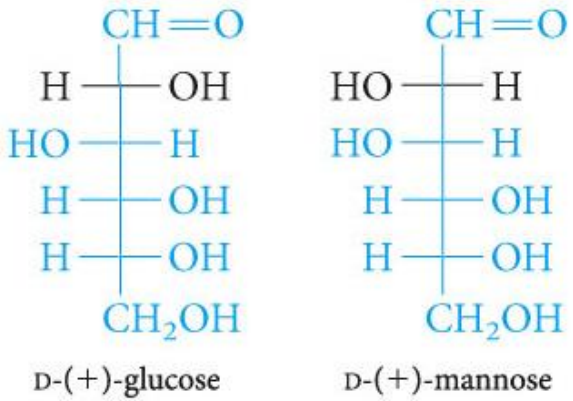


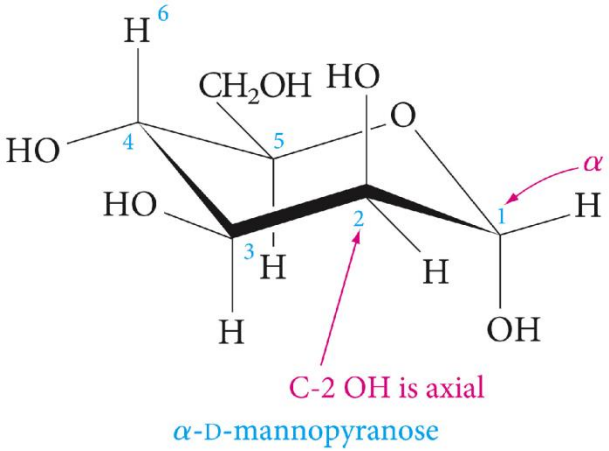
cis form



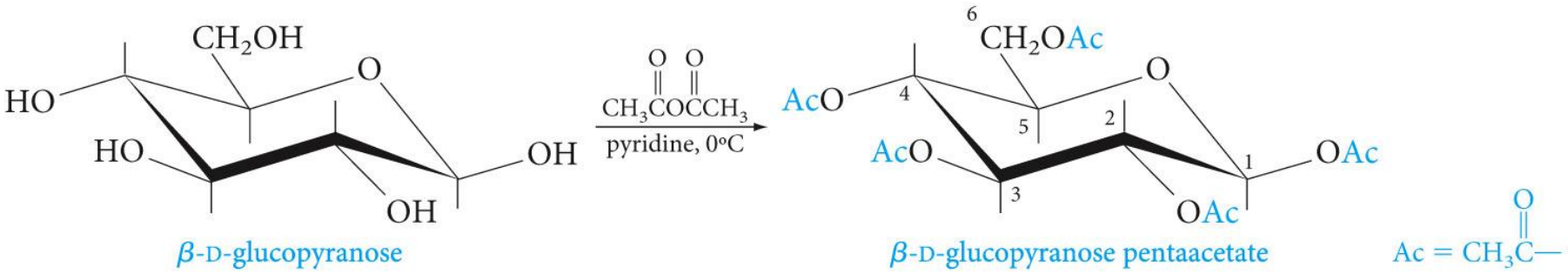
trans form

Example 5. Draw the most stable chair conformation of α-D-mannopyranose.



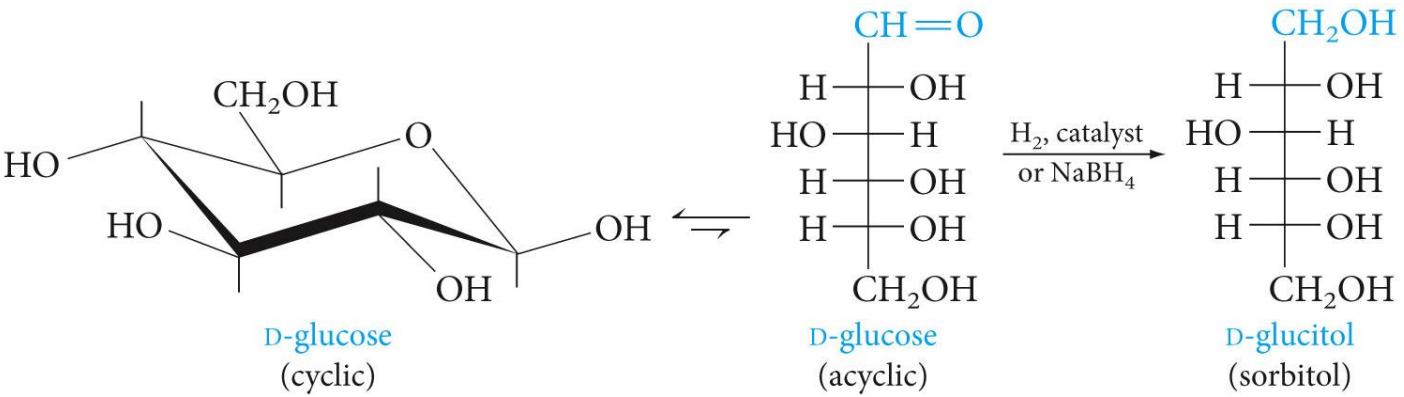


8. **Esters** and Ethers from Monosaccharides



purification and reactions in organic solvent

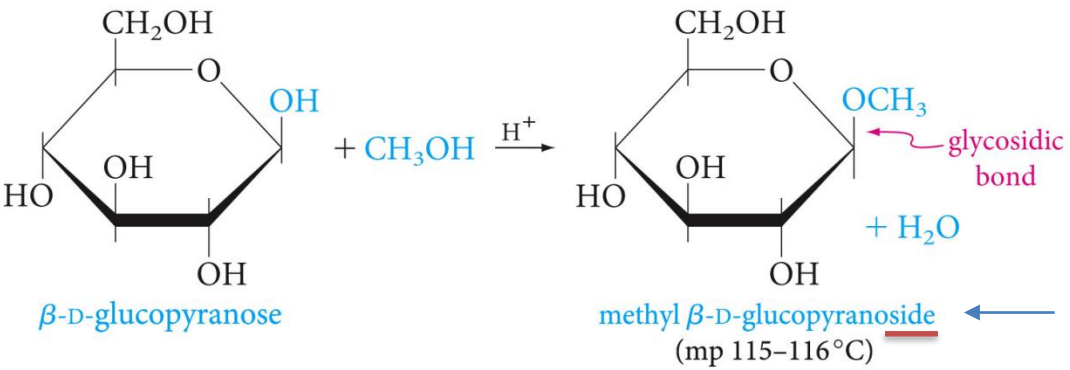
9. Reduction of monosaccharides



Catalytic hydrogenation or reduction with sodium borohydride ($NaBH_4$)

Sorbitol is used commercially as a sweetener and sugar substitute.

11. Formation of Glycosides from Monosaccharides



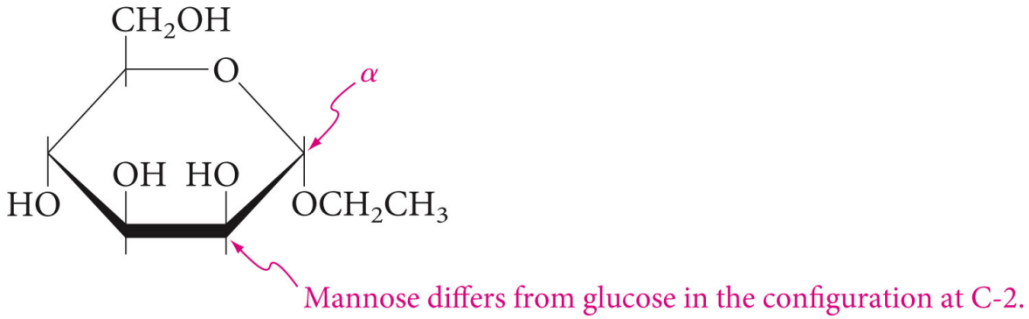
glycoside

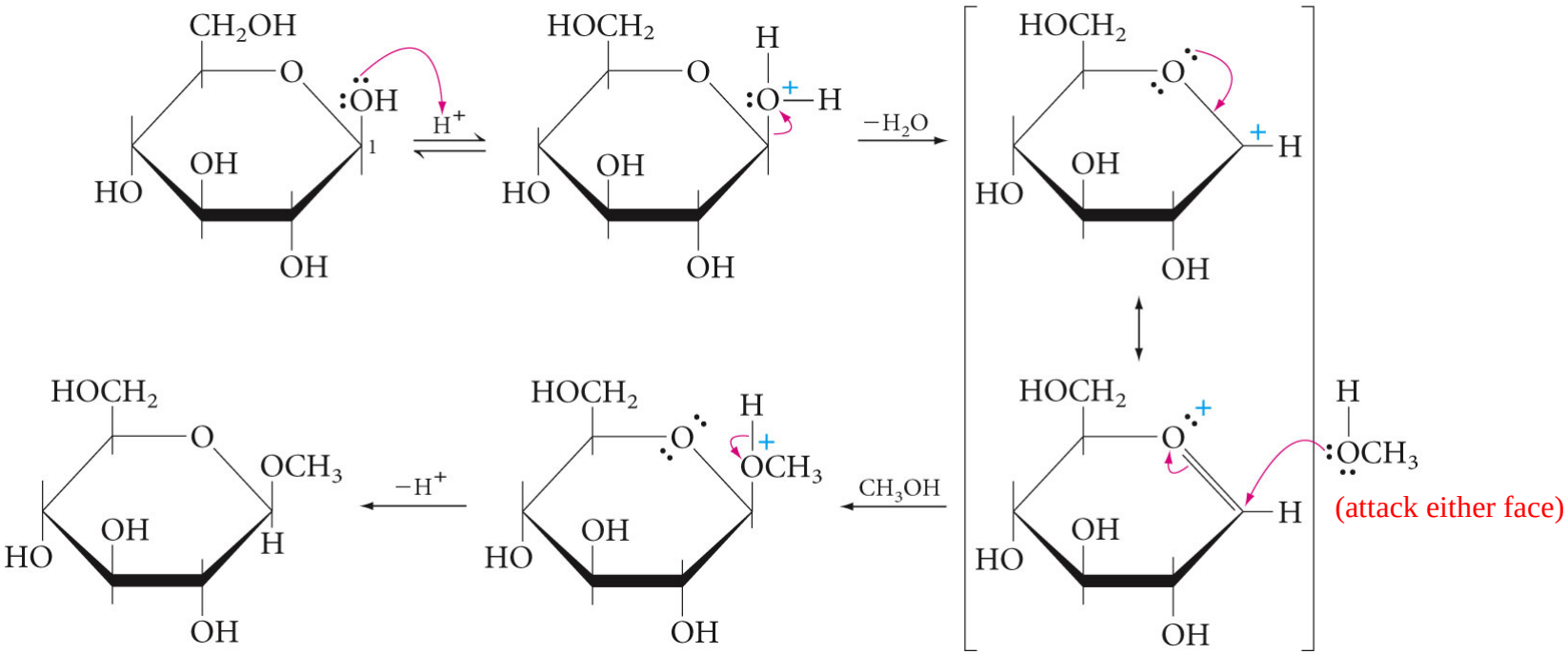
(hemiacetal)

(acetal)

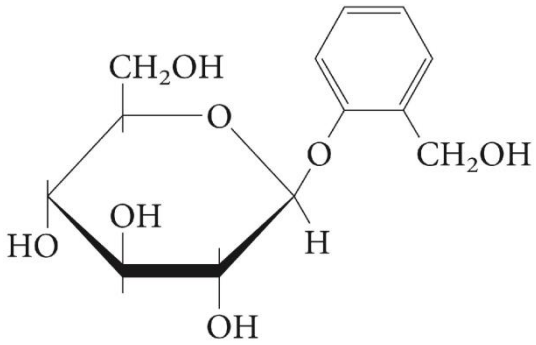
Example 16.6

Write a Haworth formula for ethyl α-D-mannoside.





beta-glycoside



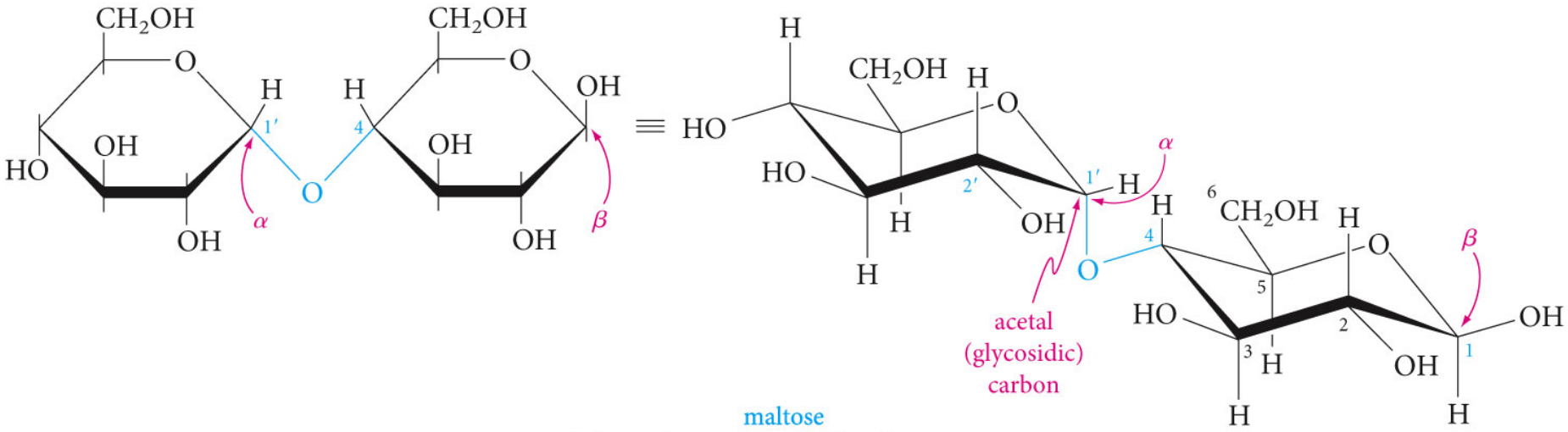
salicin

(the β-D-glucoside of salicyl alcohol)

Occurs in willow bark, fever reducing power was known to ancients

12. Disaccharides

16.12.a Maltose (엿당)



maltose
4-O-(α-D-glucopyranosyl)-β-D-glucopyranose

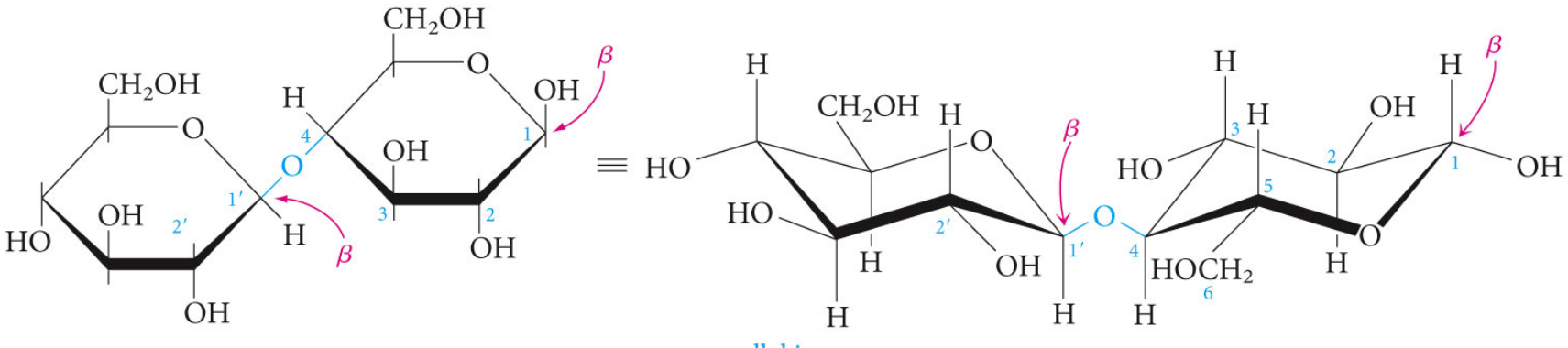
Maltose is the disaccharide obtained by the partial hydrolysis of starch.

Two monosaccharides linked by a glycosidic bond between the anomeric carbon and other hydroxyl group.

엿당은 가수분해에 의해 두 개의 포도당으로 분리가 되며, 생체 내에서는 말타아제 (maltase)에 의해 가수분해가 일어난다.

12.b Cellobiose (셀로비오스)

셀루로오스의 구성단위이다.

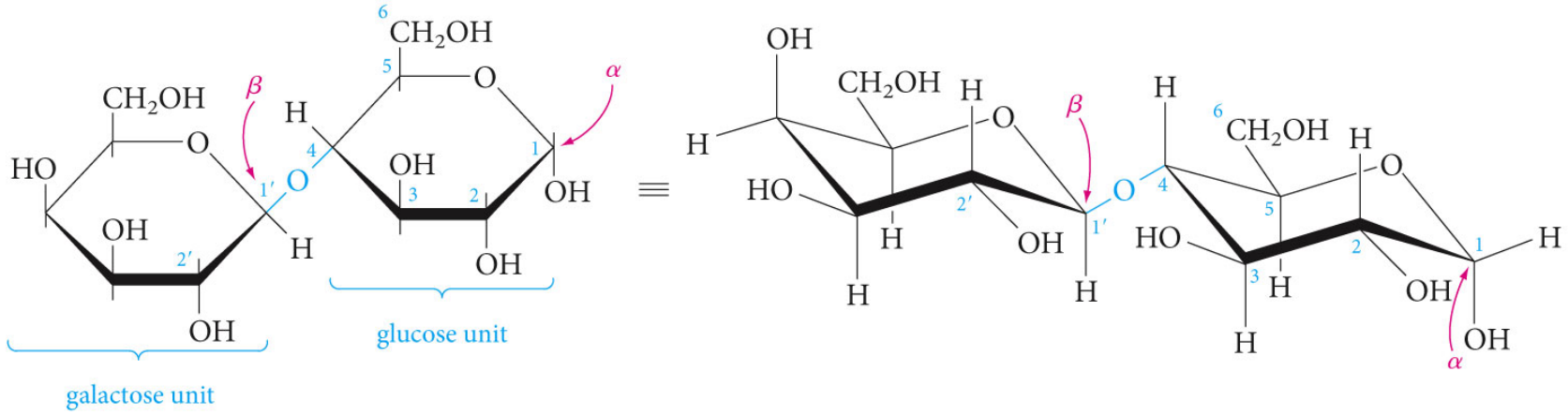


cellobiose

4-O-(β-D-glucopyranosyl)-β-D-glucopyranose

12.c Lactose (젖당, 유당)

젖당은 이름 그대로 포유류의 젖, 특히 초유 속에서 많이 발견되며, 그 양은 모유에 6.7%, 우유에 4.5% 정도 함유되어 있다.

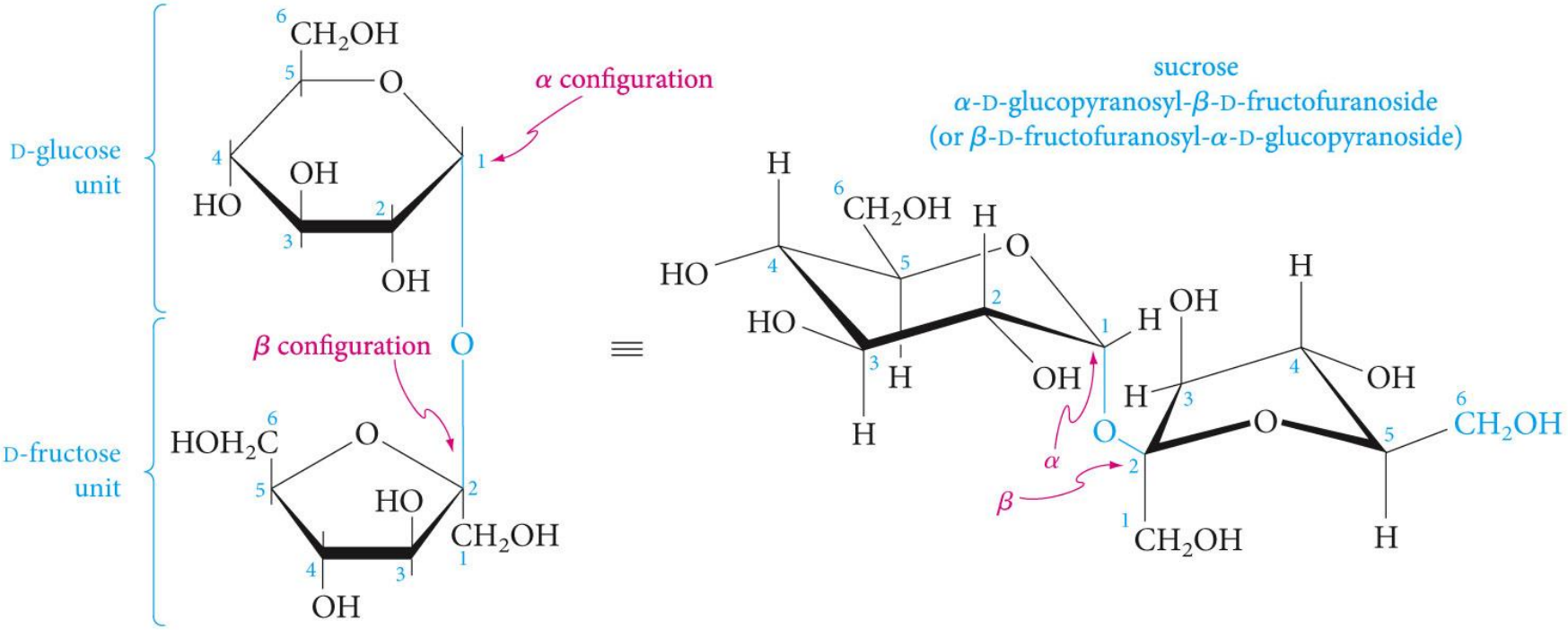


lactose

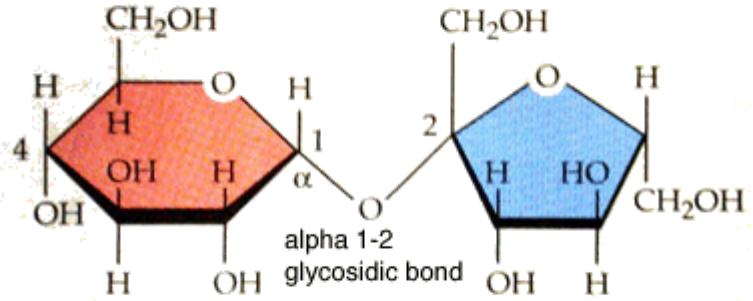
4-O-(β-D-galactopyranosyl)-α-D-glucopyranose

12.d Sucrose (자당, 설탕, table sugar)

사탕수수, 사탕 무, 당단풍 등의 즙액 중 당의 주성분이다.



Sucrose has the molecular formula $C_{12}H_{22}O_{11}$



Sucrose

Sweetness of various compounds

Name	Type of compound	Sweetness
Lactose	Disaccharide	0.16
Maltose	Disaccharide	0.33 – 0.45
Sorbitol	Polyalcohol	0.6
Glucose	Monosaccharide	0.74 – 0.8
Sucrose	Disaccharide	1.00 (reference)
Fructose	Monosaccharide	1.17 – 1.75
Steviol glycoside	Glycoside	40 – 300
Sodium saccharin	Sulfonyl compound	300 – 675
Lugduname	Guanidine compound	300,000 (estimated)